Glass Corrosion in Natural Environments

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by

Dr. Arthur N. Thorpe
Physics Department
Howard University
Washington, D.C. 20059

in conjunction with

Dr. Aaron Barkatt
Department of Chemistry
The Catholic University of America
Washington, D. C. 20064

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SECTION 1

AL-BASED LEACHANTS BUFFERED WITH ORGANIC SPECIES:

INTERACTION OF GLASS SURFACES WITH CAPS-BUFFERED MEDIA

As mentioned in the December 1991 progress report, experiments carried out involving glass samples exposed to solutions of Tris (tris(hydroxymethyl)aminomethane) at pH 8.1 have shown the appearance of "spikes" upon monitoring glass dissolution as a function of time. This phenomenon was repeated at intervals of several months. The same phenomenon was also observed in the case of glasses exposed to combinations of Tris and Mg, but higher concentrations of Mg were observed to increase the length of the interval between successive spikes. The periodic "spikes" observed in Tris-based media were interpreted in terms of cracking due to excessive stress in the surface region of the glass.

More recently, the studies on the interactions of silicate glasses with metal ions in buffered media were extended to systems containing Al, which is commonly present in groundwater, at a pH of 9.5. This pH is characteristic of groundwater present in many common geologic formations such as basaltic rock, and permits the presence of significant concentrations of dissolved Al. (The solubility of alumina, an amphoteric oxide, is at a minimum at pH 7.8.). CAPS (3-cyclohexylamino-1-propanesulfonic acid) buffer was used to establish a leachant pH of 9.5 in experiments involving the presence of Al. The experimental procedures used in this case were similar to those used with Tris-based leachants as described in

1

previous reports. Briefly, these conditions involved the use of 0.900 g of soda-lime silicate glass in each experiment with 30 mL of leachant. The leachant was one of a series of solutions containing 10, 40, 100 and 400 mM CAPS, respectively, containing 0, 5, or 50 mg/L Al and pre-adjusted to pH 9.5 with dilute NaOH. Al was introduced as $Al(NO_3)_3$ or $Na_2Al_2O_4.3H_2O$. The glass samples were exposed to aqueous media in order to study their dissolution behavior using a complete-exchange procedure based on multiple leachant replacements over a long period of time as described in previous reports.

The results of the leach experiments showed that the effect of CAPS on the dissolution of silica and other glass components from silicate glasses is quite different from that of Tris. In the absence of Al, the presence of CAPS at concentrations varying between 10 and 200 mM has no observable effect on Si dissolution at times longer than 6 months after the start of the experiments, and there is no indication of cracking (see Figure 1). In the presence of high concentrations of CAPS, amounting to 100 or 200 mM, the results obtained at times longer than 6 months show that increasing concentrations of Al in the leachant in the range of 0 - 2 mg/L reduce the extent of Si dissolution (see Figure 2). The results in this case agree with those previously observed and reported in the case of Al in Na borate buffer. On the other hand, in the presence of low concentrations of CAPS (10 or 40 mM) the introduction of up to 2 mg/L Al into the leachant has no visible effect on Si

2

dissolution. This was found to be related to the fact that relatively high concentrations of CAPS are necessary in order to keep the Al in the leachant from plating out. Analysis of the leachant blanks after 1 month of standing at 90°C showed that when 2.3 mg/L were present in the original leachant, a concentration of approximately 0.8 mg/L remained in solution at the end of the month when CAPS was present at levels of 100 - 200mM, but only about 0.3 mg/L Al remained when CAPS levels were only 10 - 40 mM. Thus, the apparent enhancement of the ability of Al to retard the glass dissolution in the presence of high levels of CAPS simply reflects the formation of an Al-CAPS complex which keeps the Al in solution until it interacts with the glass. In this respect, CAPS fulfills the same function as the citrate ion used in Ref. 14. However, high concentrations of CAPS are necessary to keep the added Al in solution, in agreement with the reported low metal binding tendency of the large, zwitterionic Good buffers.[1]

As emphasized above, the presence of CAPS, unlike that of Tris, does not cause cracking of the glass surface. This can be attributed to the fact that CAPS, unlike Tris, is an anionic buffer and therefore is not expected to react with the glass surface. Indeed, when the results obtained for the correlation between Si and Al concentrations, respectively, in CAPS-containing leachates are superimposed on those obtained in unbuffered solutions or in solutions buffered by Na borate, it is observed that there is a very good agreement among the three sets of data (see Figure 5).

The data obtained in the CAPS-buffered solutions were used to

3

compare the equivalent thickness of Al uptake as a function of time with the corresponding extent of metal ion loss. As in the case of solutions buffered with Na borate (see Figure 8a) it was not possible to obtain reliable results for the extent of Na loss because of the presence of high background Na levels resulting from the use of NaOH to adjust the pH of the CAPS solutions to 9.5. Evaluation of the extent of Al uptake showed that the former was smaller by an order of magnitude than the extent of Ca loss (see Figure 3). This conclusion remained unchanged when K was taken into account. These findings indicate that Al is not incorporated in the glass surface as a result of cation exchange, in complete agreement with the corresponding findings in the borate buffer.

SECTION 2

EFFECTS OF POTENTIAL BACKFILL MATERIALS

ON BOROSILICATE GLASS DISSOLUTION

In addition to the studies described in Section 1, which were conducted in order to understand the mechanism through which Mg and Al retard glass dissolution, preliminary studies have been initiated as to the feasibility of adding a slowly-dissolving solid compound of the additive to the glass-water system to maintain a supply of dissolved additive. In these studies, a quantity of 1 g of Defense Waste Reference Glass (DWRG, re-melted Savannah River TDS-165)[2] was placed in 40 mL of water a 90°C in the presence of 2.5 g of additive, and the leachate exchanged with fresh leachant every week for 12 weeks, then every month for 6 months. [3] (The experiments are continuing). The results of uranium analysis on the 6th monthly leachates in multiplicate tests are given in Table 1.

Table 1.   Uranium Concentrations in Leach Tests on TDS-165 Glass

Additive	Additive Grain Size mm	Uranium Concentration mg/L
1st Set		
None		0.629, 0.542, 0.666
Magnesite	0.25 - 0.355	1.949, 2.497, 2.102
Sepiolite	0.25 - 0.355	1.189, 1.142
Dolomite	0.25 - 0.355	0.185, 0.171, 0.201
Diopside	0.25 - 0.355	0.165, 0.132, 0.128
Periclase	<0.075	0.037, 0.012, -0.012
2nd Set		
None		0.631, 0.554, 0.499
Alumina	<0.075	0.786, 0.707, 0.454
Zirconia	<0.075	0.541, 0.396, 0.402
Ceria	<0.075	0.260, 0.312, 0.291
Titania	<0.075	-0.009, -0.073, -0.061

The experiments described above have now been in progress for 10 months. The concentrations of uranium in the leachates are plotted against time in Figures 4-12. In the cases of oxides which do not contain Mg (CeO_2, ZrO_2, Al_2O_3, TiO_2) the rates of uranium extraction are initially lower than in the case of additive-free water, but after a few weeks or months, the effect of the additive disappears. Among Mg-based additives, sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$) and magnesite ($MgCo_3$) consistently increase the release rate of uranium, but periclase (MgO), diopside ($CaMgSi_2O_6$) and dolomite ($CaMg(CO_3)_2$) cause a significant retardation of uranium leaching, and their effect even appears to become stronger with increasing time.

Accordingly, it appears that several magnesium compounds (dolomite, diopside, magnesia) have a suitable combination of solubility and affinity towards silicate glass surfaces to have a pronounced retarding effect on the extraction of uranium from the glass. It remains, however, to be determined how the presence of additives affects the leach behavior of glass components other than uranium.

These preliminary findings raise the possibility that introducing a magnesium source into geologic repositories for nuclear waste glass in the form of a sparingly soluble Mg-based backfill material may cause a substantial reduction in the extent of long-term glass corrosion. The studies described here also provide mechanistic understanding of the roles of various metal

6

solutes in the leachant. Such understanding forms the basis for developing long-term predictions of nuclear waste glass durability under repository conditions.

SECTION 3

MAGNETIC MEASUREMENTS ON GLASSES

From what is known about natural highly reduced glasses such as tektites, it is clear that iron is dissolved as ferrous iron with little or no ferric iron. The reducing conditions were high enough to cause metallic iron to exsolve out of the glass in the form of submicroscopic spherules. Various magnetic investigations have shown this to be the case. As the nuclear waste glass is much less reduced, a study was initiated on other natural glasses in additon to the nuclear waste glass.

We next studied glasses from Beloc, Haiti which are thought to be impact formed by under less drastic reducing conditions. Extensive measurements have been carried out on these K/T boundary glasses in order to characterize their magnetic properties. The experimental values of the Curie constant, the magnetization and room-temperature magnetic susceptibility all fall in the range of tektites. However, the temperature-independent magnetic susceptibility is about twice as high as that found for tektites. Our Mossbauer measurements show essentially no Fe^{+3} whereas other investigations find substantial amounts of Fe^{+3}. Our sample was too small to yield statistically meaningful results. Due to difficulties in obtaining sufficient amounts of sample, we are just now preparing a new and larger sample to remeasure the Fe^{+3}/Fe^{+2} ratio by Mossbauer spectroscopy. In any case, the magnetic measurements made to date indicate that most of the magnetic susceptibility is contributed by dissolved Fe^{+2} and Fe^{+3} in the glass

8

and the presence of metallic iron spherules exsolved from the glass. A small amount is contributed by paramagnetic nickel, manganese, and titanium compounds. Quantitative interpretations of the results of the measurements on the K/T glasses are still in progress and can be completed when we finish the redetermination of the Fe^{+3}/Fe^{+2} ratio. It appears that these glasses are less reduced than tektite glass.

Considerable work has also been done on several natural glasses from Yucatan, Mexico which initially were thought to be similar to the K/T glasses. These glasses, however, showed quite different magnetic properties. The temperature-independent magnetic susceptibility is very large, and the magnetization is very small but positive in some samples. However, we are able to calculate the magnetic susceptibility if we assumed there was no ferric iron. Mossbauer measurements have confirmed this assumption. The magnetic susceptibility of these glasses is contributed almost entirely by Fe^{+2} dissolved in the glass and exsolved metallic iron spherules. It appears that these glasses are similar to tektites and not to K/T glasses.

Magnetic measurements are also in progress on a new set of highly uniform simulated Savannah River glasses. These glasses have considerably different magnetic properties than any of the natural glasses. The magnetic susceptibility and Curie constant are much higher than for natural glasses. Even so, we have been able to make quite accurate calculations of the susceptibility. The experimental results on the six specimens are shown in Table 2.

Table 2. Magnetic Susceptibilities of Simulated Savannah River Glasses

Glass	Fe content, % (as Fe_2O_3)	Magnetic susceptibility, 10^{-6} emu/g
Blend 1	10.91	19.89, 19.85, 20.10, 20.20
Batch 2	11.12	19.53, 20.02, 20.37, 20.09
Batch 3	11.71	20.96, 21.42, 20.92, 21.56
Batch 4	11.71	22.42, 22.55, 22.78, 23.01
PX only		22.20, 22.69, 22.60, 22.48
HM only	7.78	16.27, 15.29, 15.81, 15.68

By assuming all of the ferrous iron is in solution, that part of the ferric iron which contributes to the Curie constant can be calculated. By further assuming that the Fe^{+3} iron, which is not in solution, is in the form of finely divided Fe_2O_3 in the glass, the magnetic susceptibility can be calculated. The calculated values agree closely with the measured values. For example, the calculated value for Blend 1 (see Table 2) is 20.01 x 10^{-6} emu/g which is close to the experimental values.

As all these nuclear waste glasses were produced under conditions where the bulk of the iron is in ferric form, the apparent correlation between iron content and susceptibility is an effective method of monitoring glass composition.

10

CONCLUSIONS

Among organic buffers, Tris causes cracking of the glass
surface, resulting in spectacular "spikes" when dissolution rates
are monitored as a function of time. The presence of Mg, which
stabilizes surface, increases the intervals between consecutive
"spikes". CAPS, on the other hand, shows no deleterious effects on
the glass surface and even promotes surface stabilization by Al
since CAPS keeps the Al in solution until it reacts with the glass.

REFERENCES

1. N. E. Good, G. D. Winget, W. Winter, T. N. Connoly, S. Izawa and R. M. M. Singh, Biochemistry, $\underline{5}$, 467-477 (1966).

LEGENDS TO FIGURES

Figure 1. Si concentrations in the leachates resulting from glass dissolution in dopant-free CAPS solutions, $S/V = 290$ m^{-1}.

Figure 2. Si concentrations in the leachates resulting from glass dissolution in Al-containing 200-mM CAPS solutions, $S/V = 290$ m^{-1}.

Figure 3. Equivalent layer thicknesses for Si matrix dissolution, net Ca loss, and Mg uptake
   a.   in 5-mg/L Al leachant buffered with 10 mM Na borate, $S/V = 290$ m^{-1}
   b.   in 2-mg/L Al leachant buffered with 200 mM CAPS, $S/V = 290$ m^{-1}.

Figure 4.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of CeO_2.

Figure 5.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of ZrO_2.

Figure 6.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of Al_2O_3.

Figure 7.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of TiO_2.

Figure 8.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of sepiolite, $Mg_4Si_6O_{15}(OH)_2*6H_2O$.

Figure 9.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of magnesite, $MgCO_3$.

Figure 10.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of periclase, MgO.

Figure 11.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of diopside, $CaMgSi_2O_6$.

Figure 12.   Uranium concentrations in leachates obtained in complete-exchange tests on DWRG at 90°C in the presence of dolomite, $CaMg(CO_3)_2$.
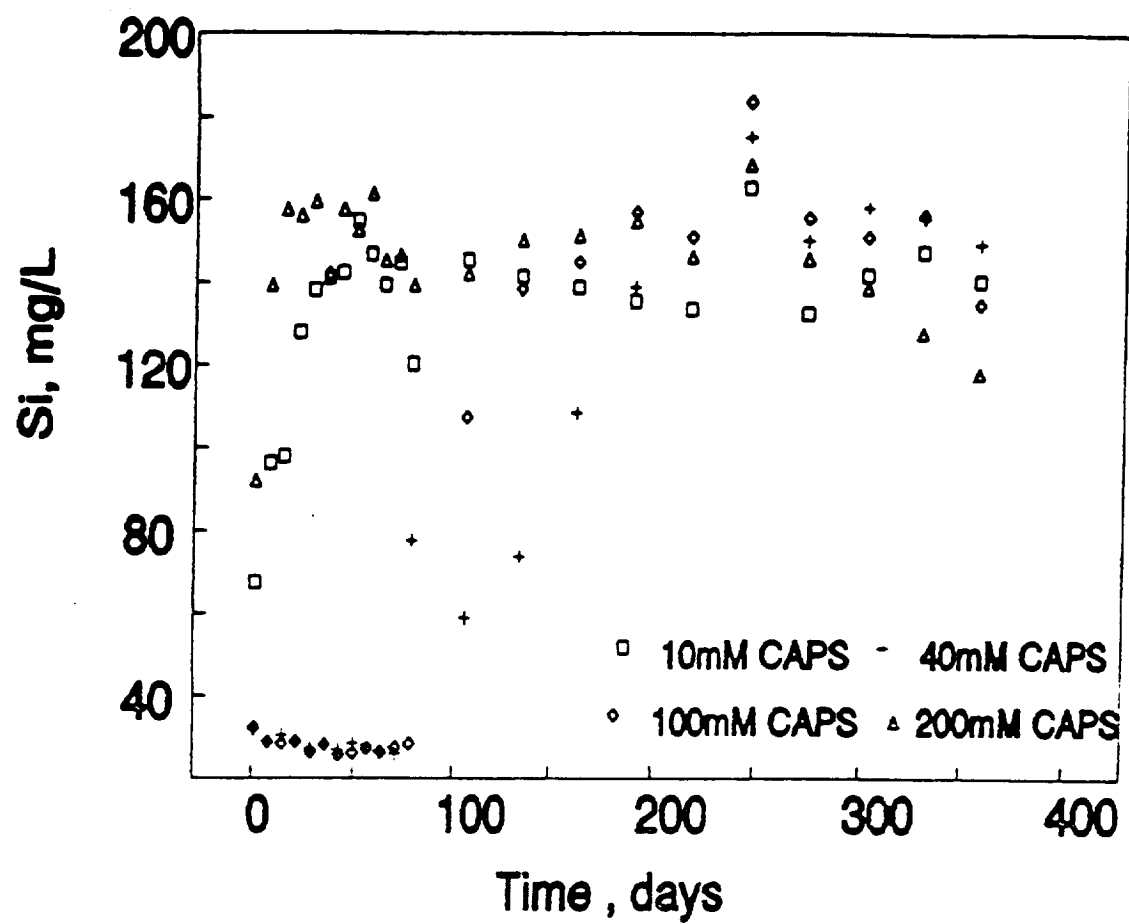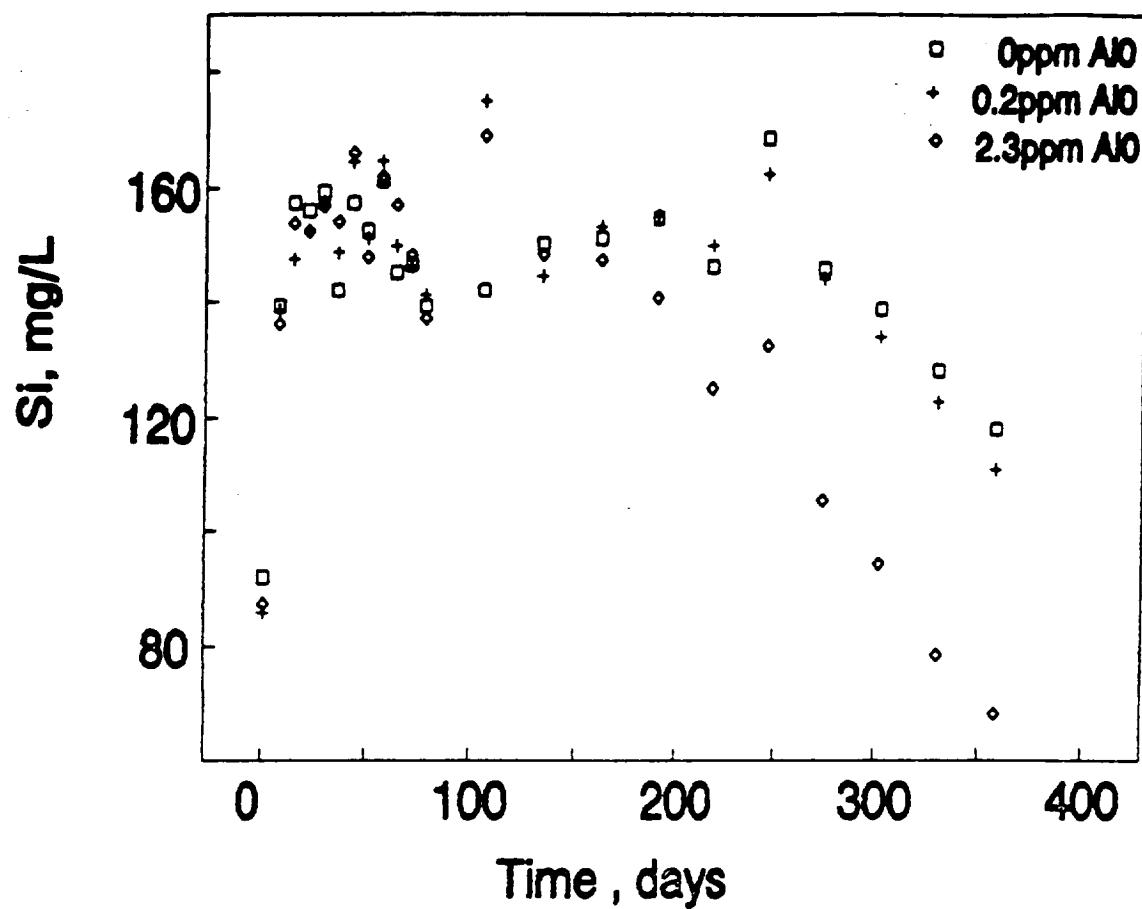
Figure 3a

Figure 3b

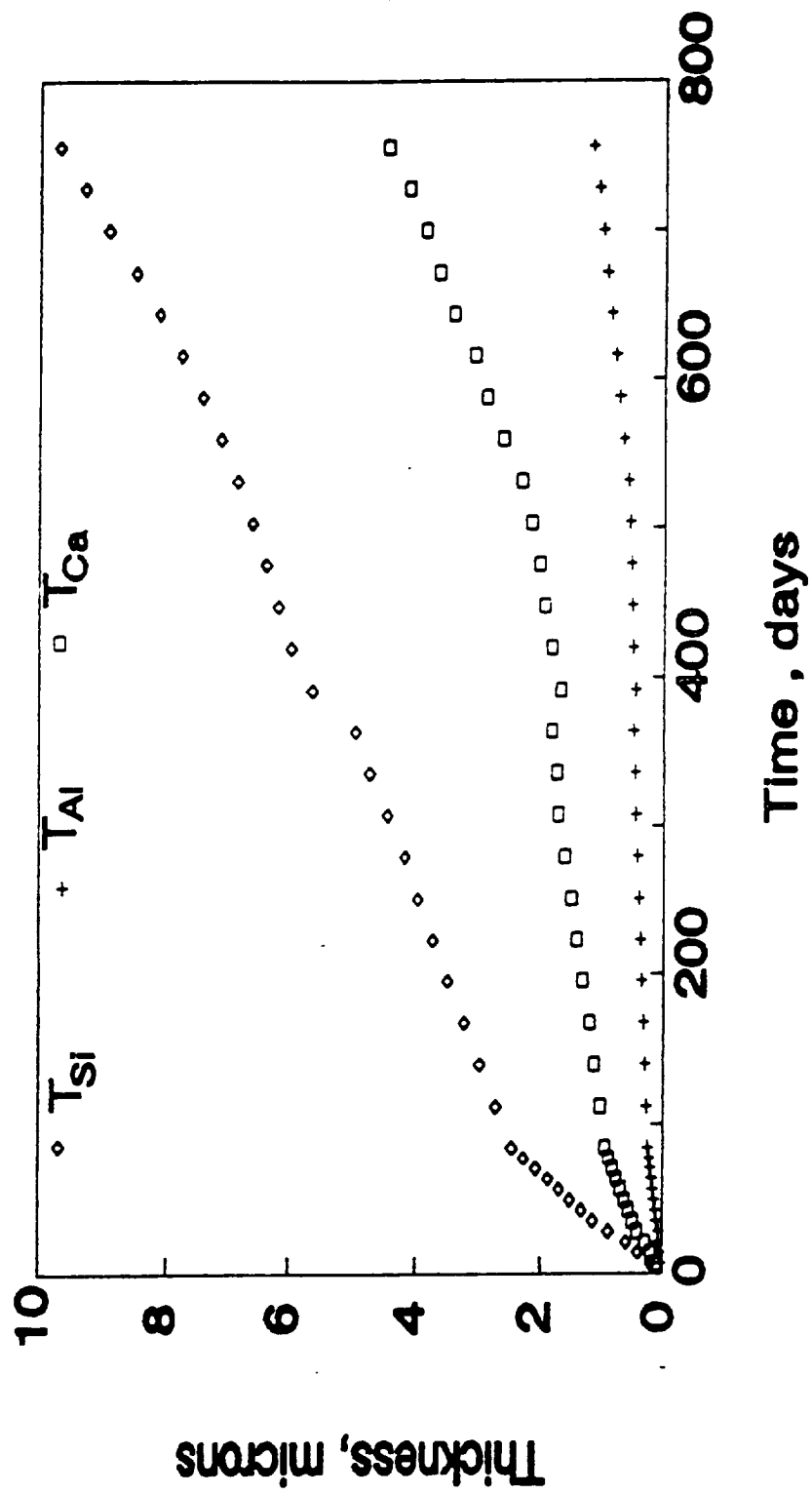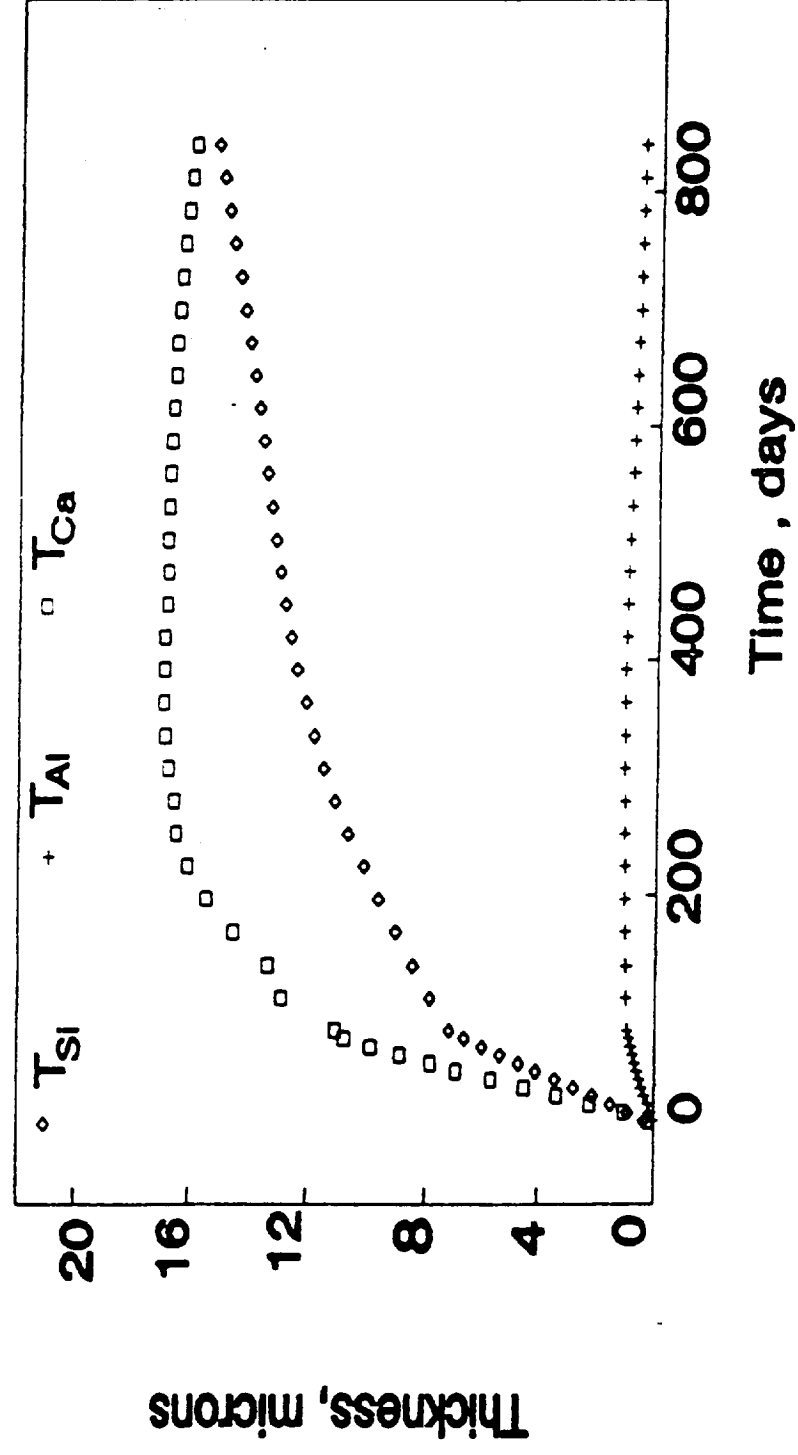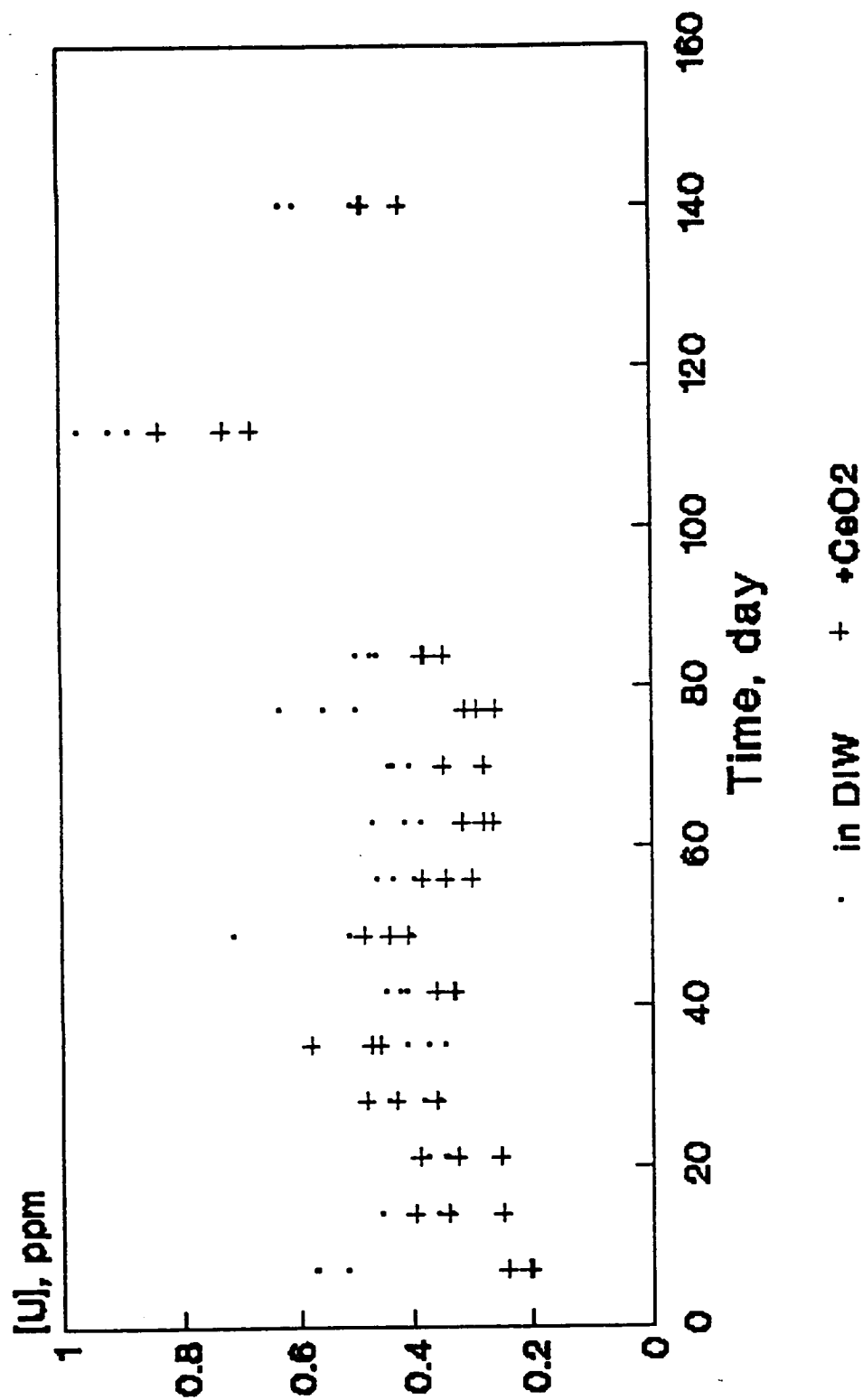Figure 4

DWRG powder in DIW w/o CeO2
Triplicate experiment

[u], ppm

Time, day

· in DIW   + +CeO2

Figure 5

DWRG powder in DIW w/o ZrO2
Triplicate experiment

[u], ppm

Time, day

· in DIW   + +ZrO2
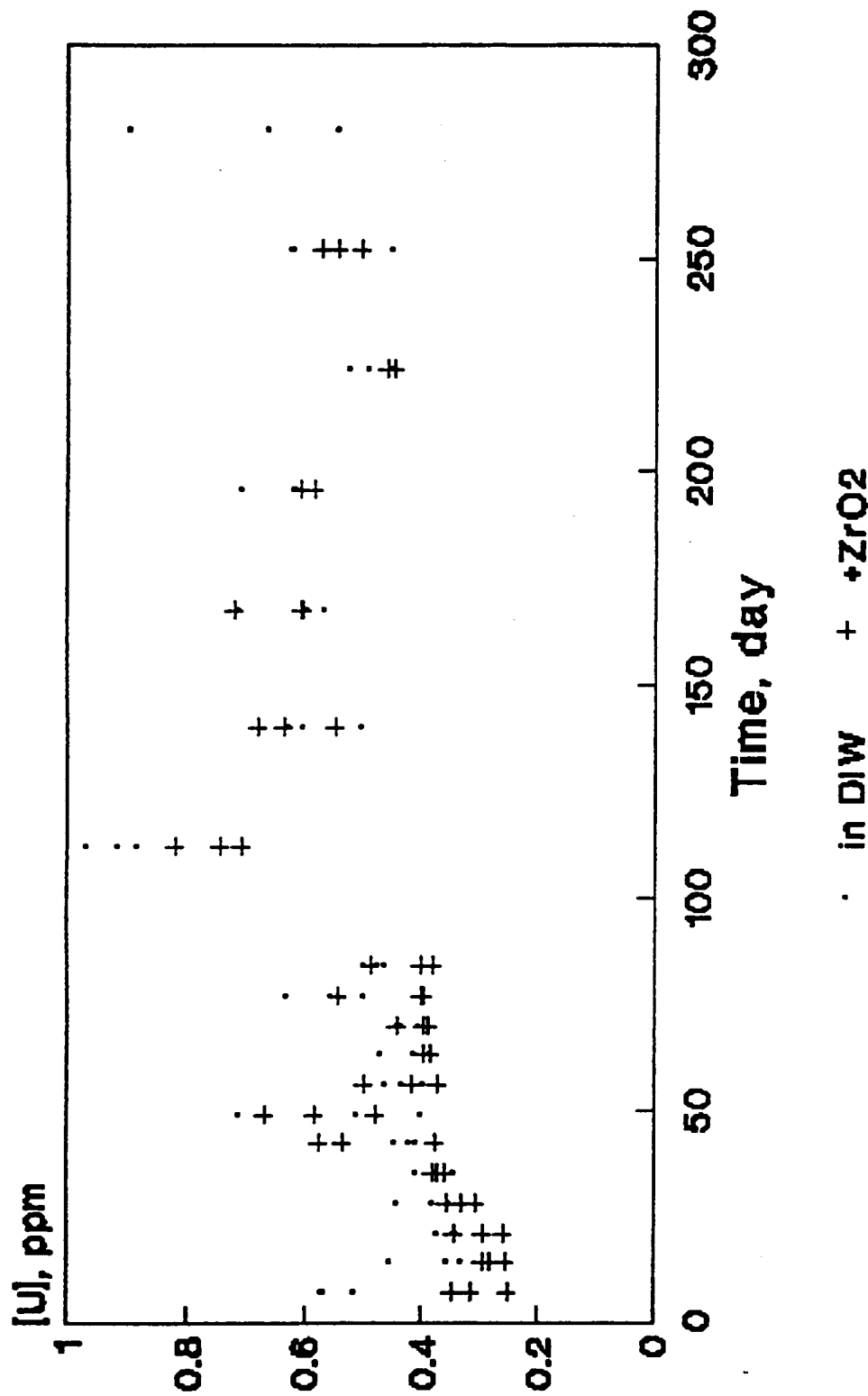
Figure 6

DWRG powder in DIW w/o Al2O3
Triplicate experiment

[U], ppm

1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0

0   50   100   150   200   250   300

Time, day

·   in DIW   +   +Al2O3
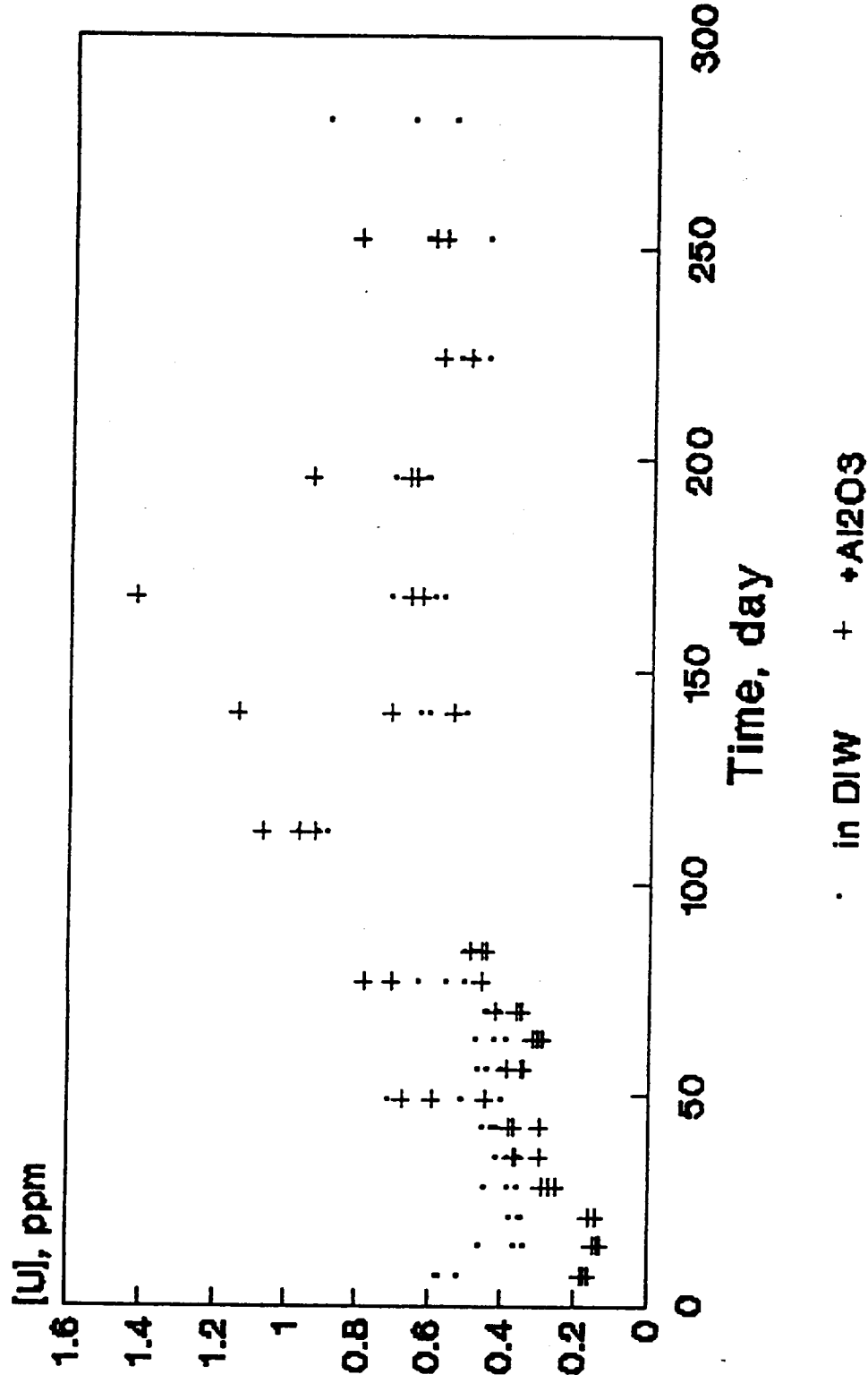
Figure 7

DWRG powder in DIW w/o TiO2
Triplicate experiment

[u], ppm

Time, day

· in DIW   + +TiO2
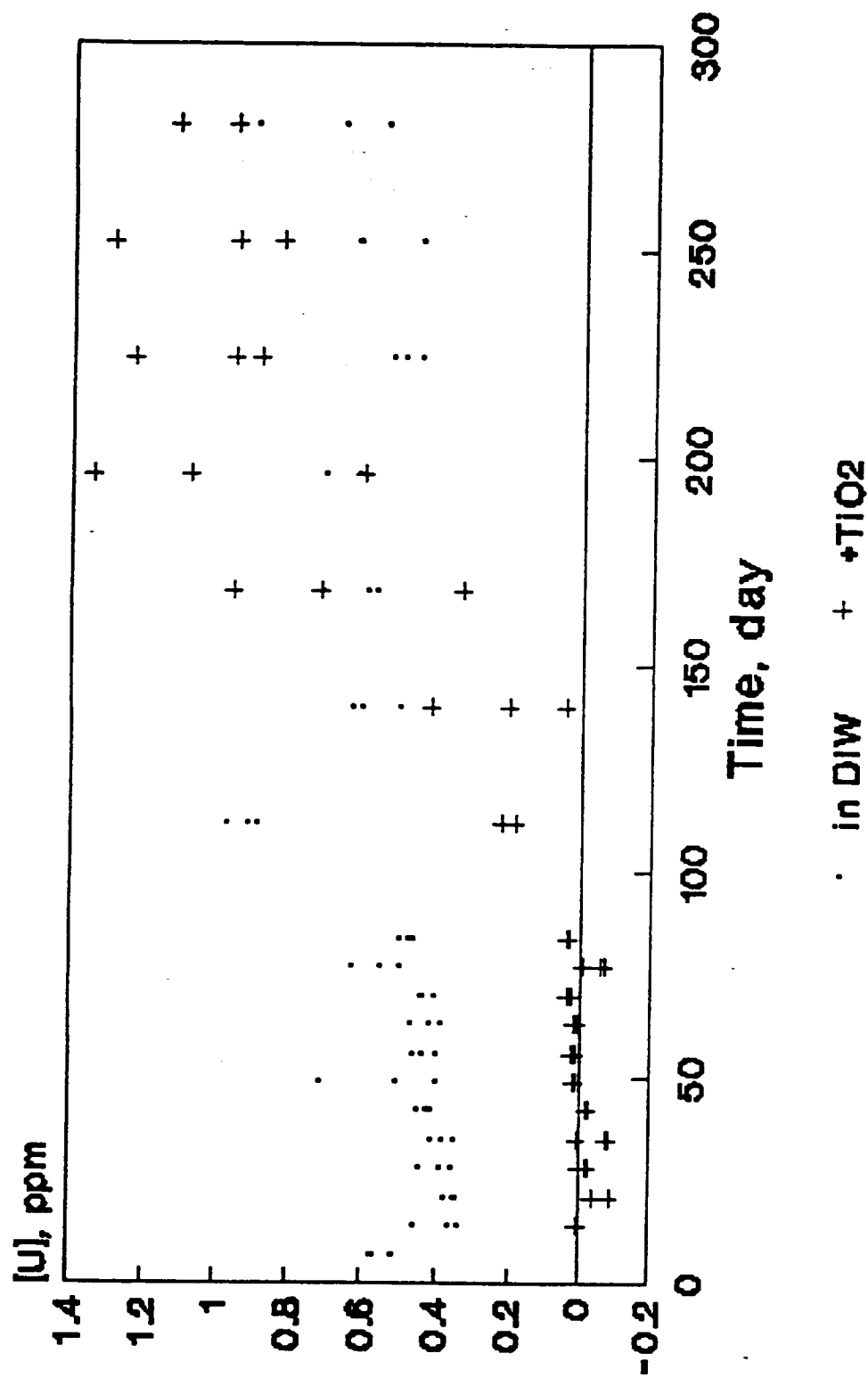
Figure 8

DWRG powder in DIW w/o sepiolite triplicate experiment

[U], ppm

Time, day

· in DIW   * +Skp
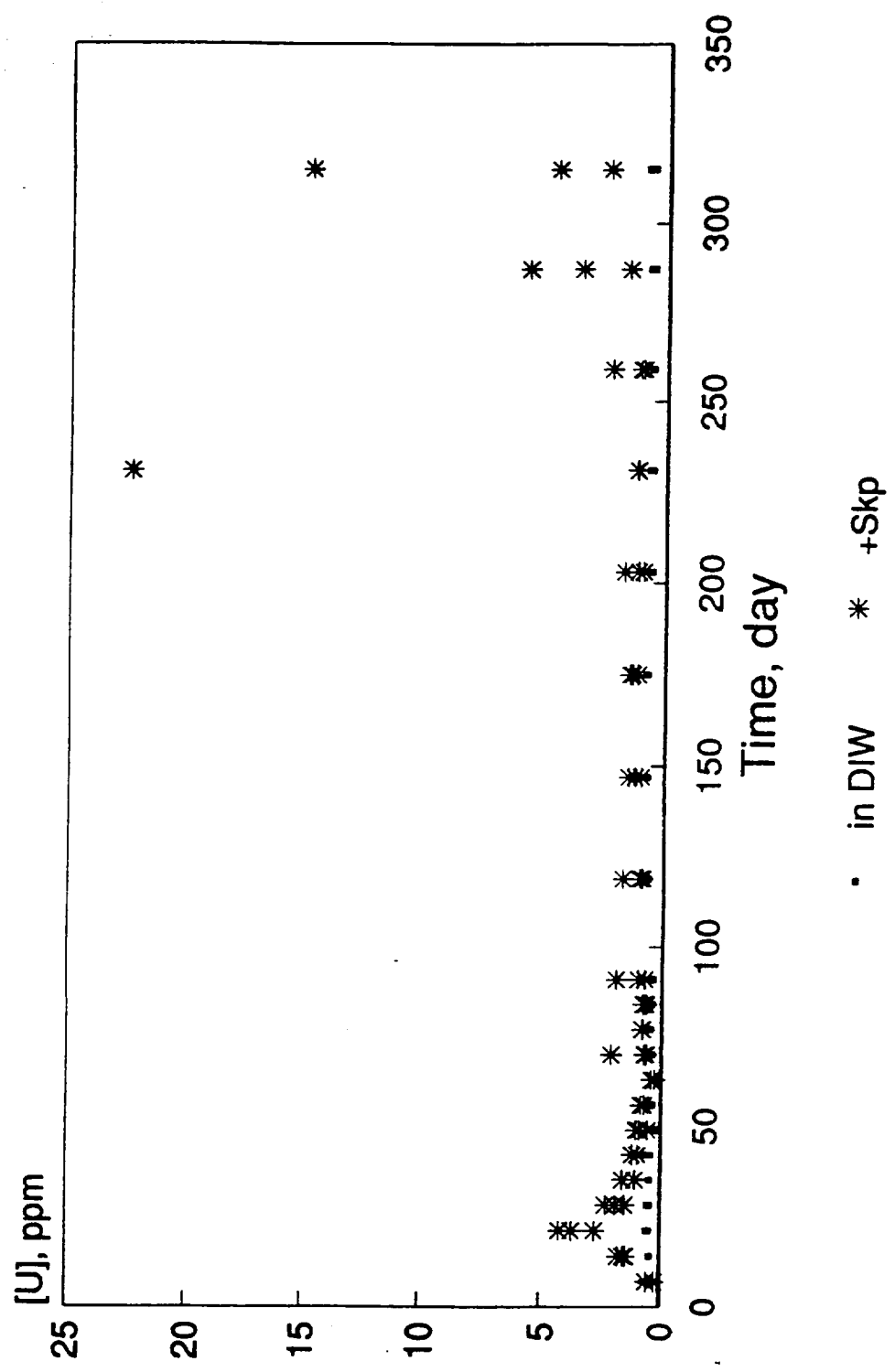
Figure 9

DWRG powder in DIW w/o magnesite triplicate experiment

[U], ppm

Time, day

• DIW   × +Mag
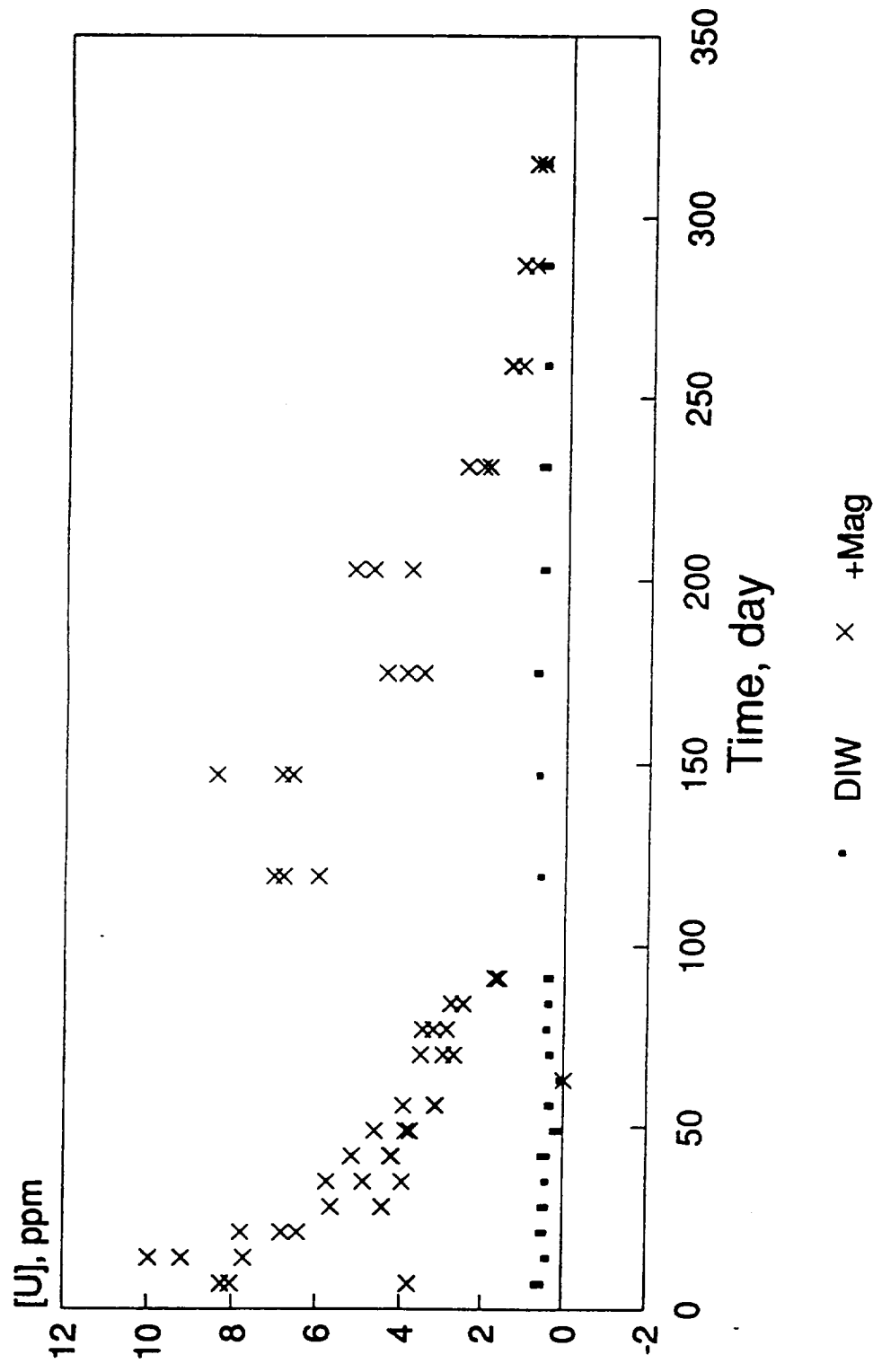
Figure 10

DWRG powder in DIW w/o MgO
triplicate experiment
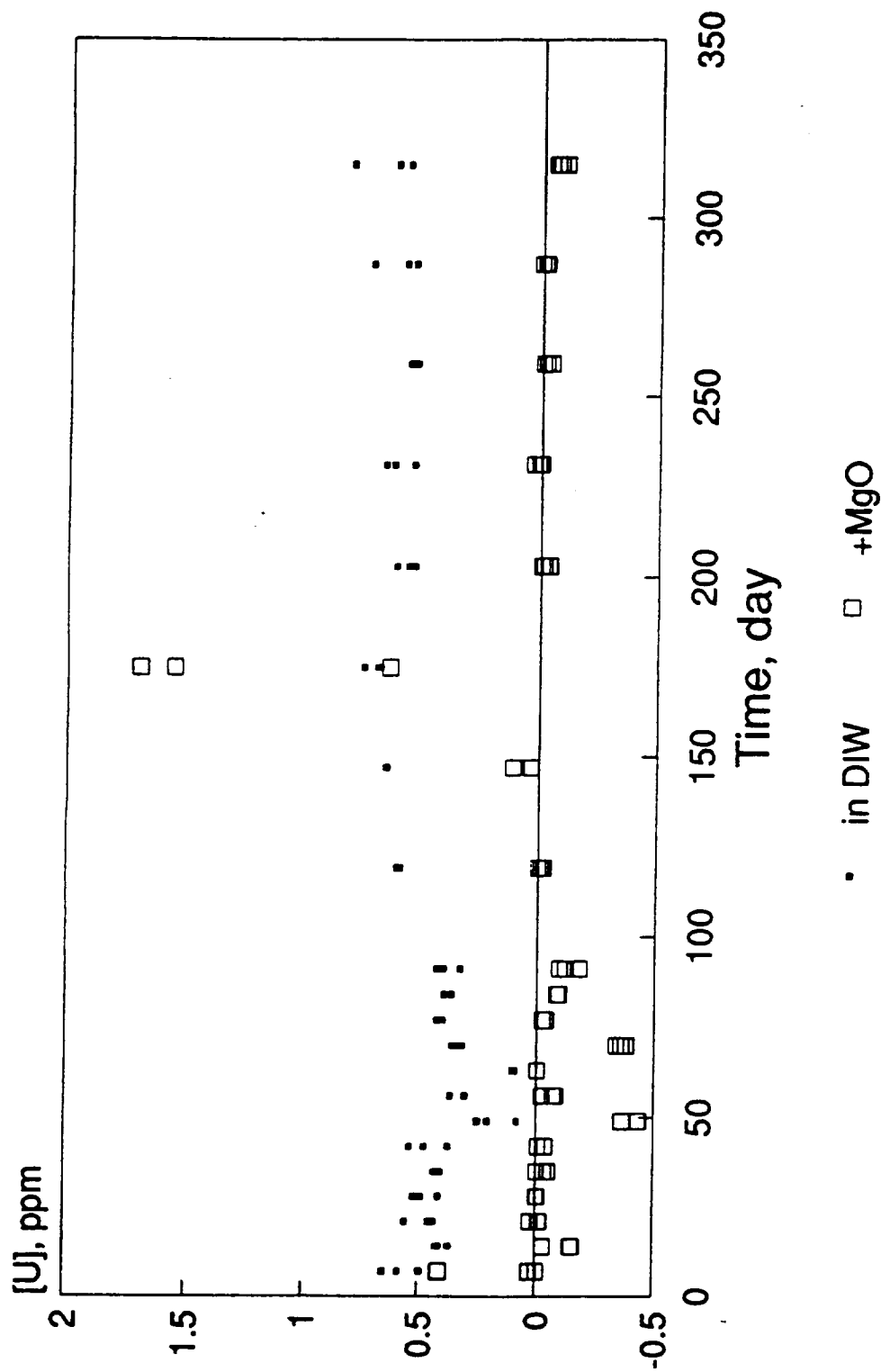
[U], ppm

Time, day

· in DIW   □ +MgO
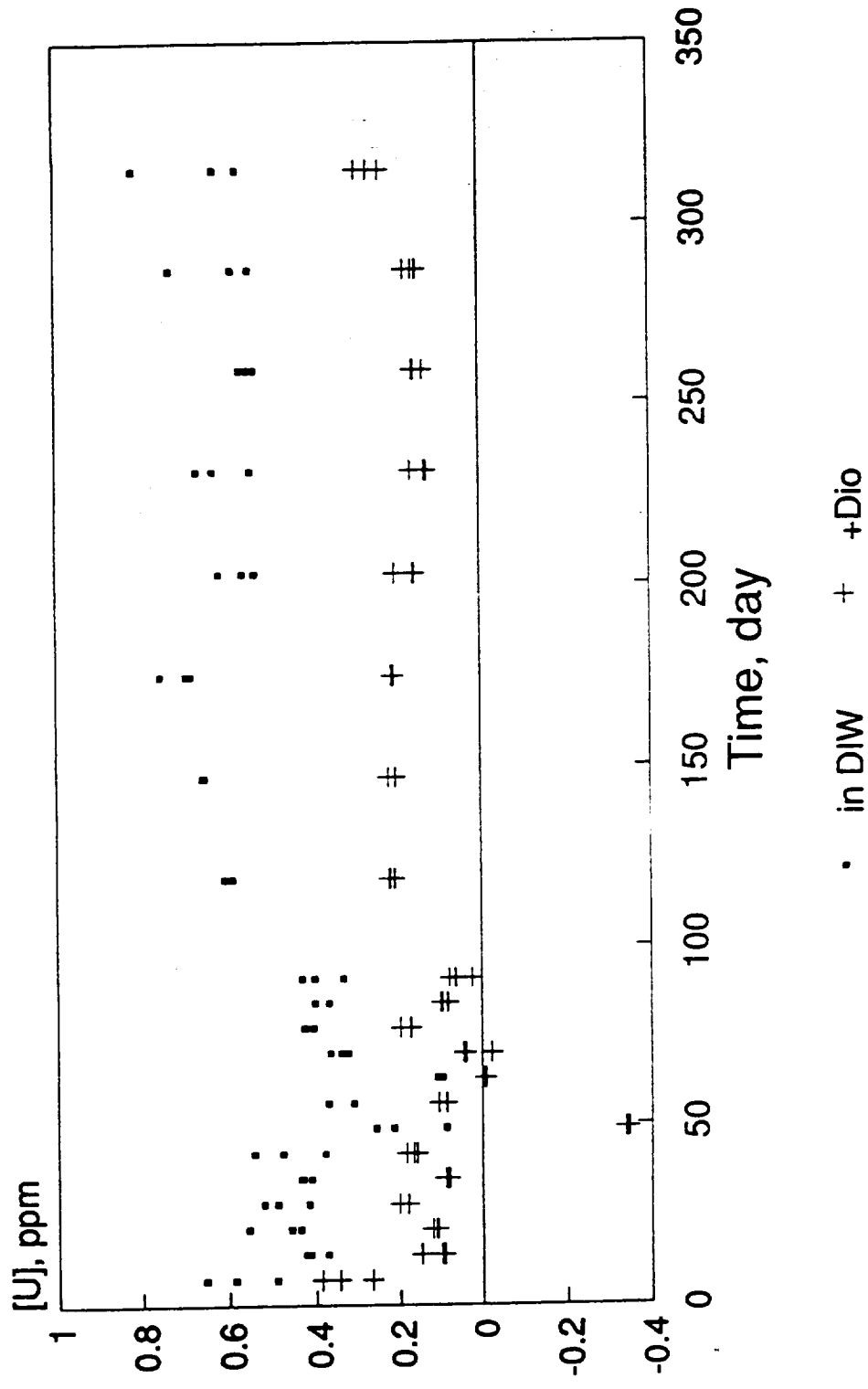
Figure 11

DWRG powder in DIW w/o diopside triplicate experiment

Figure 12

DWRG powder in DIW w/o dolomite triplicate experiment

Time, day

[U], ppm

· in DIW   ◇ +Dol